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By-products of palm oil mill effluent treatment plant – A step towards sustainability

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ABSTRACT

The current wastewater treatment system for palm oil mill effluent (POME) regularly fails to treat the effluent efficiently. The growing demand for palm oil has caused a substantial increase in the generation of POME. To meet the discharge limit proposed by the Department of the Environment, the POME must be treated effectively before being released into the receiving water bodies. The open pond system is presently being used to treat the POME because the open pond system is cheap and less maintenance is required. However, the failure of this technique in the current scenario has spurred the research into new technologies to explore their applicability in treating POME. Although the discovery of new technologies is commendable, the financial infeasibility of these new treatment techniques has stagnated their progress. In this work, a role for the by-products of the treatment systems in implementing the new technologies with return of investment has been revealed. A thorough review of the characteristics and recent trends for producing polyhydroxyalkanoate (PHA), a by-product, is also discussed in this work. Moreover, the opportunities available to further enhance the production of PHA in POME wastewater have been addressed and are presented in this work. Production of biohydrogen, another by-product, is also discussed in this review. In a nutshell, the enhancement of PHA production coupled with biohydrogen production as a by-product may provide a new dimension to the POME treatment plant by generating revenue. Production of PHA and biohydrogen from POME contributes significantly towards the cause of sustainability.

Contents

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1. Introduction

An industrial wastewater treatment plant is generally considered a money depletion zone in a business operation. Little investment would therefore be made in the wastewater treatment plant. As a result, the wastewater is either insufficiently treated or not treated at all. If this trend continues, the environment will be severely polluted, and access to clean water will be limited in the future. An increase in the volume of industrial wastewater has been reported in developing countries [1]. The increase in the volume of industrial wastewater in developing countries can be related to the growth of the population. Population growth causes the demand for end products to increase. Similar developments can be expected for palm oil derivative products. An increase in the demand for end products causes the production rate to increase and concomitantly increases the amount of wastewater released into water bodies. Fig. 1 shows the projected world population growth for developing countries and industrialised countries. An exponential increase in world population is expected in developing countries in another 30 years.

Developing countries such as Malaysia, Indonesia, Nigeria and Thailand are the major force in supplying palm oil to the world [3]. Fig. 2 shows the palm oil producers in the world. In particular, the oil palm industry is the fourth largest contributor to the Malaysian economy, contributing approximately RM 53 billion of the Gross National Income of Malaysia [4]. This industry has grown in tandem with the nation's growth. The production of palm oil contributes approximately 39% of the total palm oil production in the world, and 44% of the palm oil is exported around the world [5]. Essentially, the palm oil demand grows because palm oil is cheap and has high oxidative stability. Biodiesel production from palm oil has recently escalated the demand for palm oil further. With the growing demand for palm oil, the plantation area of oil palm trees has reached approximately 5 million hectares in Malaysia [6]. The crude palm oil (CPO) production was 18.8 million tonnes in 2012. Under the Tenth Malaysian Program, the palm oil is expected to contribute approximately RM 69.3 billion through exportation [7].

In tandem with the increase in demand for palm oil, CPO production rate has escalated approximately 171% in the span of 20 years in Malaysia (as shown in Fig. 3). Higher CPO production has increased the amount of waste released from the oil extraction process, and this waste has a critical need to be addressed. Empty fruit bunches, press fibre, palm kernel endocarp, palm kernel press cake and liquid effluent (palm oil mill effluent (POME)) are the wastes generated through processing to produce CPO [9]. These wastes cause detrimental effects to environmental quality if they are left untreated. Among those wastes, POME makes up the largest portion. For every 1 t of CPO, approximately 5–7.5 t of water are necessary. More than 50% of this water that is used in the production of CPO will end up as liquid waste [10]. POME characteristics as determined by different researchers are presented in Table 1. Table 1 shows that POME is evidently an agent causing severe pollution (high chemical oxygen demand (COD) and the presence of oil and grease). The critical need to treat the POME has sparked the interest among researchers to find new

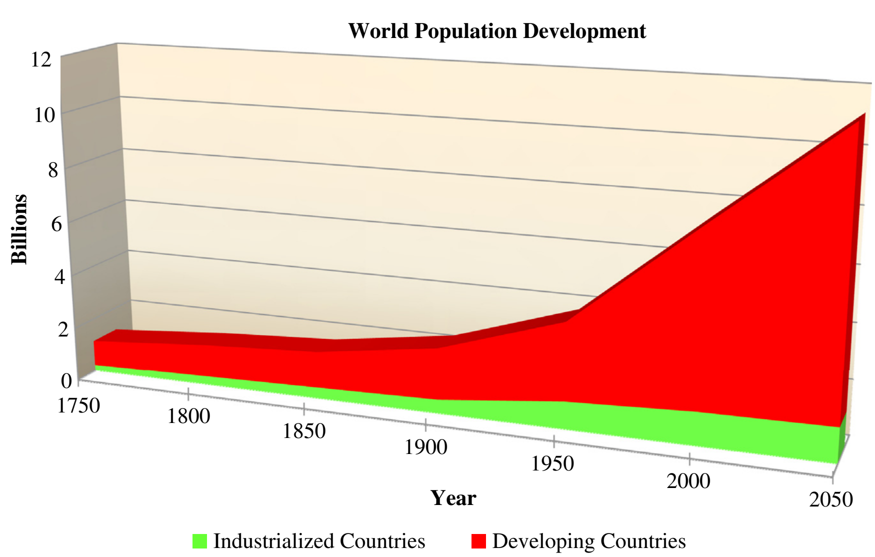

Fig. 1. Projected population of the world [2].

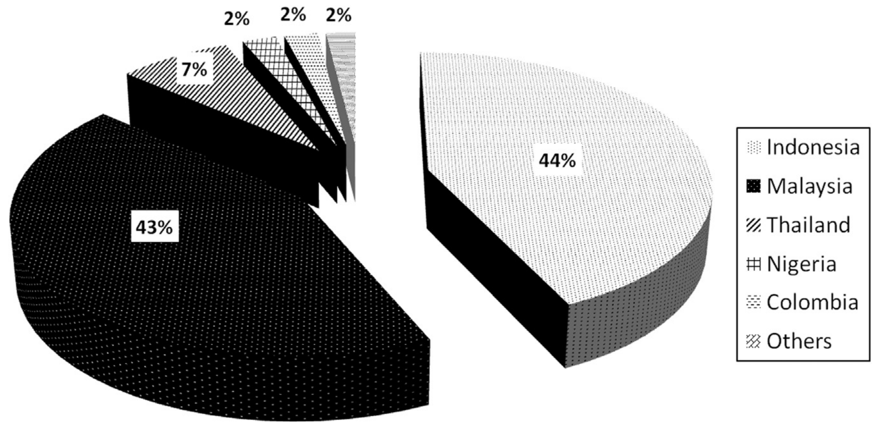

Fig. 2. World palm oil producers [8].

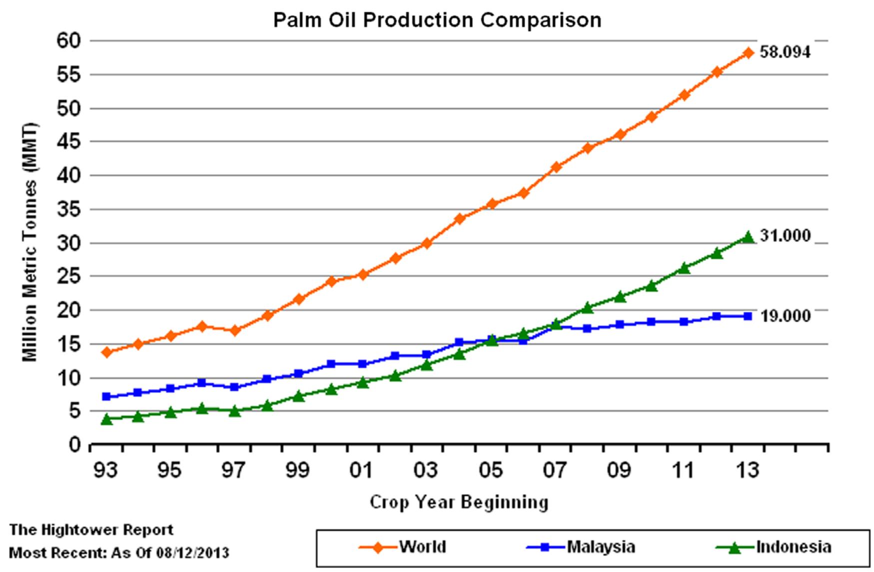

Fig. 3. Crude palm oil production amount [11].

Table 1
Characteristics of POME from various previous studies.

pH	BOD (mg/L)	COD (mg/L)	Oil and grease (mg/L)	Suspended solids (mg/L)	Nitrogen Content (mg/L)	Reference
3.5–4.5	11,000–30,000	30,000–70,000	5000–13,000	9000–25,000	500–900	[12]
5	11,000	246,000	–	–	–	[13]
4.7	25,000	50,000	4000	18,000	750	[14]
4.52	–	70,900	–	25,800	–	[15]
4.0–4.8	–	30,000–50,400	1300–4700	11,500–22,000	660–890	[16]
3.5–4.2	10,000–44,000	16,000–100,000	–	5000–54,000	–	[17]
4.15–4.45	21,500–28,500	45,500–65,000	1077–7582	15,660–23,560	300–410	[18]
5.6	–	46,000	–	42,800	–	[19]
5.5	–	35,000–50,000	–	35,000	–	[20]

efficient treatment methods. The treatment method must complement the increasing growth of the CPO production rate and comply with the demand of the Department of the Environment (DOE) to release waste to the environment within safe parameters.

POME is generally treated using series of large shallow ponds (biological treatment system). The ponds cannot be very deep, so large reaction volumes are obtained by increasing the surface area. The restriction on depth is mainly because there is difficulty in oxygen penetration to the bottom of the pond if the pond is deep. Therefore, large land areas and long HRTs (approximately 40 days) are required for the series of aeration ponds to treat the POME effectively [21]. However, this technique is considered obsolete and as a result, POME is being treated ineffectively. The failure of the treatment system is caused by the sensitivity of the microorganisms present in the treatment ponds towards climate changes (related to temperature changes) and pH fluctuation [14]. The series of shallow ponds also occupies a large land area, releases obnoxious gases such as hydrogen sulphide and methane openly to the environment and has a long hydraulic retention time (HRT) [22]. By addressing the hazards posed by POME, various efforts have contributed towards the improvement of the POME treatment system.

The obsolete open pond method has been the stimulus either to explore new technologies or to modify the existing treatment

technology. Through intensive research, a number of innovative technologies to treat the POME have been found. Physical and chemical treatment systems such as membrane technology are among the new technologies used to treat the POME [23–25]. The results of these technologies are highly encouraging (COD removal of approximately 96.5%) [24]. However, the newly invented technologies remain at laboratory scale without seeing much progress to industrial scale because a high cost is required to operate a sophisticated treatment system compared to the current ponding system. Difficulty in upscaling the laboratory-scale technologies also contributes to the lack of new technologies applied at the industrial level. A profitable and feasible technology is desired to cause new treatment technologies to be implemented on an industrial scale. Most of the innovative technologies fail in terms of financial feasibility [26].

Failure of the innovative technologies to be upscaled has led to attention reverting to biological treatment method. However, new perspectives must be found to make the biological treatment method feasible in terms of treatment efficiency as well as financial sustainability. One of the attractive new approaches is to transform the POME treatment plant into an income-generating source rather than an investment depletion zone. Income could be generated through the trading of by-products from the wastewater treatment plant. Most of the by-products are largely underutilised and their economic potential is yet to be exploited. Nevertheless, the by-products could be generated only through a systematic treatment system. A systematic and efficient treatment system would ensure that the POME is treated efficiently and simultaneously generate income through the by-products. Return of investment (ROI) from the wastewater treatment plant is a win-win situation for the mill operation as well as the environment.

With these considerations, this review will focus on the by-products from POME that have been reported in previous work. First, the available POME treatment methods and their by-products will be discussed. The current utilisation and the potential uses of the by-products will be reviewed in this work. This review will also determine the appropriate treatment method to treat POME efficiently and to simultaneously produce by-products that have return of investment value. Profitable by-products from wastewater may attract a palm oil mill to invest in a wastewater treatment plant. Production of profitable by-products would ensure that wastewater treatment could achieve its goal, suppress the operating cost to a minimal level and concurrently protect environmental quality. Current constraints in producing by-products and future work are discussed in this review.

2. POME treatment methods

2.1. Methods to treat POME

To chart a new dimension for a POME treatment plant (or for any agricultural wastewater), the available and currently used treatment methods must be understood. By understanding the current treatment methods, a relevant solution could be found and implemented in the future. POME is generally treated in various ways at industries. These treatment methods have been in use for decades, and their efficiency is widely variable.

2.1.1. Biological treatment

In the current scenario, biological treatment is the commonly used method in industries due to its low cost, high organic loading capability, and simple and low energy demand [25]. Microorganisms present in the treatment system will degrade the biodegradable substances, which in turn reduces the COD of the wastewater. The anaerobic treatment is preferred at the beginning stage of the POME treatment process due to the ability of the anaerobic treatment to reduce the COD and the BOD rapidly in the absence of oxygen [27]. As aeration is not needed, an anaerobic treatment reduces the operating costs. During the anaerobic process, a sequence of reactions occurs, namely, hydrolysis, acidogenesis and methanogenesis [28]. For anaerobic treatment, series of open ponds have commonly been used to degrade the POME. The open ponds consist of a de-oiling tank, acidification ponds, anaerobic ponds and facultative or aerobic ponds [22]. The ponding system has been in practice to treat the POME since the mid-1980s [29]. At present, 85% of the POME treatment is based on the anaerobic and facultative ponding system [10]. However, the effluent from the pond system was not able to meet the DOE discharge standards even after 80 days of retention time. The COD and biochemical oxygen demand (BOD) for the final effluent of the aerobic pond were 1725 mg/L and 610 mg/L, respectively [29].

Drawbacks of the open pond system led to other biological technologies that were tested for POME treatment. Borja and Banks [30] have treated the POME with an upflow anaerobic sludge blanket reactor (UASB). The results from the treatment showed that up to 96% of the COD was removed. The UASB reactor also has a noteworthy advantage over the ponding system because the hydraulic retention is much shorter (1.5–3 days), and the area required for the UASB reactor is smaller. One of the salient features of the UASB is the formation of granular sludge [25]. However, the UASB could not retain an adequate amount of microorganisms for the high loading treatment. Consequently, the experiment was conducted in an upflow anaerobic filtration (UAF) for POME treatment [31]. The necessity of introducing the UAF is to retain the denser microorganisms in the reactor, which eventually allows efficient treatment of the higher loading of POME. In the UAF method, almost 90% of the substrate was oxidised, and the operation of the reactor was reported to show good stability under acidic and alkaline conditions [31]. Unlike the ponding system, the UASB or UAF can capture the methane in the reactor. Methane gas can be utilised as an energy source to power the palm oil processing mill, subsequently saving the operating cost of the mill. Methane is produced in the methanogenesis step of the anaerobic reaction. The organic compounds in POME will be converted into methane and carbon dioxide by methanogens. For every 1 g of COD removed from the POME, 0.69–0.79 dm^3 of methane gas is produced in the UAF [31]. Despite the production of methane, the common problem associated with the UAF is malfunctioning at a high organic loading rate due to the presence of suspended solids in the POME [25]. To overcome this shortcoming, the integration of the UASB with the Upflow Fixed Film (UFF) reactor was proposed and used successfully to treat the POME on a laboratory scale [25]. The integrated reactor is called the upflow anaerobic sludge fixed film (UASFF) reactor. The schematic diagram of the UASFF is shown in Fig. 4. Through the UASFF reactor, the retention of solids would be higher and improve the solid/liquid/gas separation in the reactor. The 97% COD removal (reactor was operated at 3 days HRT) was achieved by using this reactor [25]. However, this technology could not be implemented at the industrial level because of the failure of the upscaling process.

Apart from the anaerobic treatment techniques for POME discussed earlier, research has been performed on aerobic treatment as well. The major drive for aerobic treatment research is to reduce the hydraulic retention time of the anaerobic POME treatment. Vijayaraghavan et al. [32] have investigated the aerobic treatment of POME using an activated sludge reactor. They reported that the COD removal achieved for aerobically treated POME was 98% for a hydraulic retention time of 60 hours. Compared to the work done by Borja and Banks [30], almost 96% COD removal could be achieved with a shorter hydraulic retention

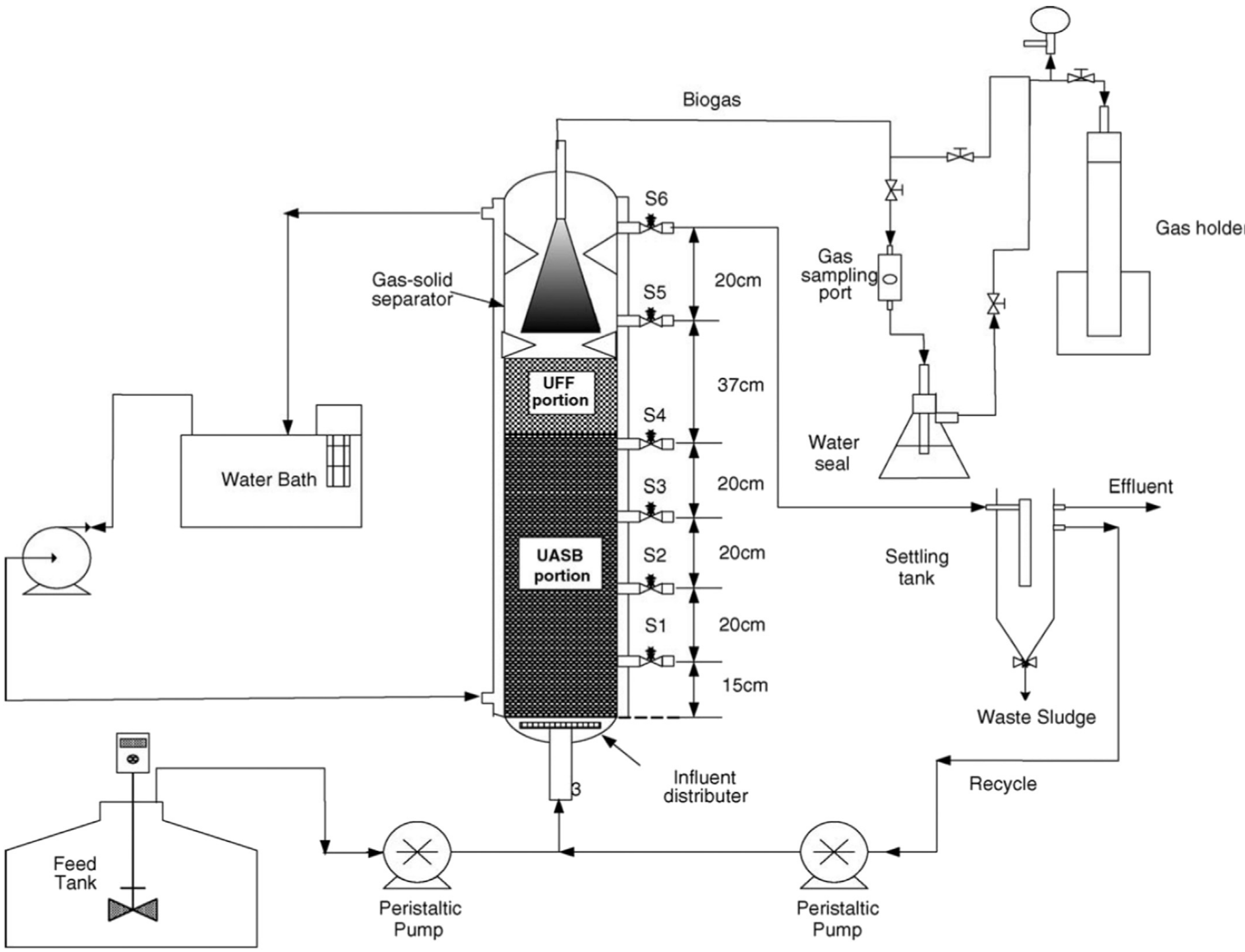

Fig. 4. Schematic diagram of UASFF [25].

time for POME treatment using an aerobic system. Meanwhile, the use of aerobic digestion of POME decreases the carbon content and inorganic nitrogen whilst changing the pH from acidic to alkaline [33]. Although aerobic treatment offers a method with a shorter retention time, the aerobic treatment also has drawbacks. In the method used by Vijayaraghavan et al. [32], the presence of biomass in the effluent poses problems for the receiving water body. These problems paved the way for the development of aerobic granules for treating POME. Gobi et al. [20] have successfully developed aerobic granules in POME and simultaneously used these aerobic granules to treat POME. Aerobic granules have good settling ability in addition to being robust in nature [34] and enable the effluent to be biomass-free. Work done by Gobi et al. [20] differs from the work of Vijayaraghavan et al. [32] in terms of the reactor setup as well as the biomass morphology. Emphasis was given to establishing a greater height over diameter (H/D) ratio in the reactor operated by Gobi et al. [20] to promote the formation of aerobic granules in the reactor. The sequencing batch reactor (SBR) system used by Gobi et al. [20] occupies a small footprint compared to the activated sludge reactor. The comparison in terms of the morphology of the biomass used is shown in Fig. 5. The conventional activated sludge (as a seed sludge for granular formation) used by Gobi et al. [20] is shown in Fig. 5(i). Meanwhile, the fully developed aerobic granules could be seen in Fig. 5(ii). Another salient feature of the SBR aerobic granule system is the hydraulic retention of POME. The SBR aerobic granule system requires only 24 h for the POME to be treated with 90% efficiency. Though the granulation could be promising, aeration could increase the overall operating cost.

2.1.2. Non-biological treatment

Apart from biological treatment methods, several alternative methods were found that could be used to treat the POME. Among these alternative methods are coagulation–flocculation, adsorption, membrane technology, and integrated technologies. In the coagulation–flocculation treatment method, several types of chemicals have been used to destabilise the colloids in the POME. Chemicals such as polyacrylamide derivatives, aluminium sulphate and polyaluminium chloride have been used as coagulants and flocculants for POME treatment [35]. In the coagulation–flocculation treatment system, only the suspended solids would be separated from the POME wastewater. The coagulation–flocculation treatment system does not reduce the COD value significantly. The adsorption technique is limited to removal of the residual oil in POME and used as a final polisher. The effectiveness of the adsorption technique in reducing the COD is evidently not reported [36,37]. Apart from low COD removal, both coagulation–flocculation and adsorption techniques could not be used comprehensively to treat the POME due to the maintenance and operating cost [17]

As far as membrane technology is concerned, the results obtained from the experimental work appear to be excellent. Ahmad et al. [14]

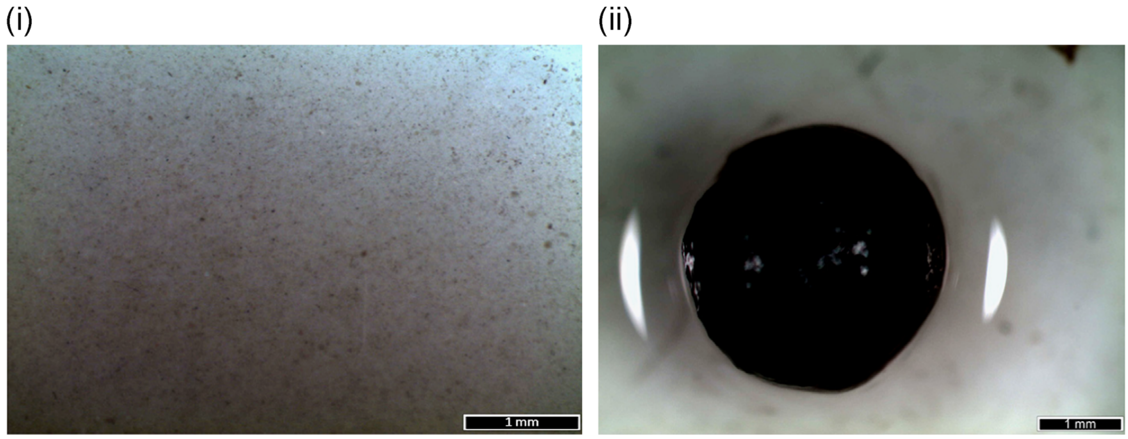

Fig. 5. Morphological comparisons between (i) activated sludge and (ii) aerobic granules for POME treatment [20].

have reported that 99% of the influent COD was removed from the raw POME. However, prior to the membrane treatment, POME must be pre-treated with several techniques. In the study done by Ahmad et al. [23], POME underwent three stages of pre-treatment. The function of these three stages was to partially reduce the turbidity, COD and BOD before the membrane treatment. In each stage of the membrane treatment, either chemical or external energy is needed to produce the final effluent, which directly raises the operating cost of a treatment plant. By acknowledging the shortcomings of a membrane treatment method for POME, a comparison of overall operating costs has been conducted with different setups of the membrane treatment system. The lowest cost of the three setups studied was RM 7.03/m^3 [38]. The membrane treatment system is still considered high end technology compared to the biological treatment method [39], but implementation of the membrane technology at the industrial level has been unsuccessful.

2.1.3. Integration of biological and non-biological treatment

Zhang et al. [17] have integrated biological treatment with the membrane separation system. The first stage of the treatment consist of an expanded granular sludge bed (EGSB) and an aerobic reactor. The second stage of treatment consists of an ultrafiltration membrane and reverse osmosis membrane. This treatment system is capable of producing biogas energy as well. The effluent produced at the end of the treatment system was almost crystal clear and could be used as boiler feed water [17]. A similar concept of recycling the water has been investigated by others as well [14,23,40]. Chaiprapat and Laklam [41] have integrated an ozone pre-treatment system with an anaerobic treatment system. The break-down of recalcitrant components in POME by ozone would ease the subsequent anaerobic treatment system. The anaerobic sequencing batch reactor (ASBR) was reported to manage to treat the POME efficiently at high organic loadings (9.04 kg COD m^{-3} day^{-1}), shorter cycle times (12 h) and longer hydraulic retention times (10 days). In another work, Chan et al. [42] integrated anaerobic and aerobic technologies into a single bioreactor for the treatment of POME. This technique is indeed a fresh approach in terms of reducing the land area needed for the inefficient ponding system. Ideally, a single reactor could be used for the POME treatment because anaerobic and aerobic treatment could be carried out in the same reactor. The removal efficiency reached more than 99% in terms of BOD and TSS removal. In addition to the high removal efficiency, 0.42 L/g COD of methane gas is produced in this bioreactor. Though the long term implications and operation of this reactor are still being evaluated, the early results from this reactor look promising. However, the presence of biomass in the effluent was not addressed in their work. Choi et al. [43] used an anaerobic hybrid reactor (AHR), anaerobic baffled filter (ABF) reactor and an anaerobic downflow filter (ADF) reactor in a single system for the treatment of POME. The main purpose of this treatment method was to sustain a high ratio of effluent recycling as well as to reduce the retention time for the POME treatment. This technology has managed to remove 95.6% of influent COD at an OLR of 13 kg COD m^{-3} day^{-1}. The combination of the anaerobic reaction and the filtration process helps to maintain the effluent clear of biomass. Moreover, as a result of the anaerobic process, methane gas was produced at 0.171 and 0.269 L CH_4/g COD removed.

POME could be treated in various ways. The choice of treatment system depends on the capital cost as well as the concern of the operators about the environment. The summary of POME treatment methods and their respective COD removal is given in Table 2.

2.2. Summary of POME treatment methods

All of the methods reported exhibited various degrees of efficiency in terms of treating POME. Clear comparison in terms of advantages and disadvantages of the methods used to treat POME is given in Table 3. Nevertheless, the biological treatment is still preferred by the mill operators as it is cheap and requires less maintenance. However, considering the impact of the effluent on nature, many alternatives research efforts have been conducted, as discussed in the previous section.

Thus, to strike a fine balance between safeguarding the environment and keeping the operational cost of the POME treatment low, industrially feasible solutions must be decoded. The most obvious issues with the currently implemented biological treatment system (series of ponds) are the occupancy of large areas and the release of obnoxious gases to the environment. These issues could be resolved with either altogether new technology or improvements to the biological treatment system. However, investment is needed for the new technology or improvement to occur. Taking the necessary investment into consideration, return of investment from the new technologies or improved technologies would be an exciting prospect that can be explored. Return of investment from the treatment plant could be generated by marketing the by-products. By-products from treatment plant are an added boon for the investors in palm oil mills. Moreover, if the by-products can replace any non-sustainable raw materials for the production of end products, this type of replacement would contribute significantly towards sustainability. Production of marketable by-products could give a new dimension altogether for a treatment plant. More investment can be expected in the treatment methods as well as pledging the efficient treatment of wastewater. Ultimately, production of

Table 2
POME treatment methods and COD removal.

Treatment methods		Details	COD removal (%)	Reference
Biological treatment	• Anaerobic	• Pond	65	[29]
		• UASB	90	[30]
		• UASFF	97	[25]
	• Aerobic	• ASR	98	[32]
		• SBR	90	[20]
Physical treatment	• Membrane technology	–	99	[14]
	• Microbial fuel cell	–	96.5	[24]
	• Adsorption	• Rubber powder	NA	[36]
		• Chitosan	NA	[35]
		• Activated carbon	17.45	[37]
Chemical treatment	• Coagulation–flocculation	• Moringa oleifera seeds	52.2	[44]
Integration technology	• Biological-membrane	–	93	[17]
	• Ozone-anaerobic treatment	–	NA	[41]
	• Anaerobic–aerobic	–	99	[42]
	• Anaerobic-filtration	• AHR–ABF–ADF	96.5	[43]

NA – Not available.

Table 3
Comparison between various treatment methods of POME.

Methods	Advantages	Disadvantages	References
Membrane treatment system	• Excellent pollution removal efficiency	• Costly treatment system • Needs high maintenance • High pressure is required	[14]
Biological-membrane integrated system	• Excellent removal performance	• Costly treatment method	[17]
Microbial fuel cell	• Generation of electricity • High removal performance	• Difficult to scale up • Costly treatment method	[24]
Upflow anaerobic sludge fixed film (UASFF)	• Small footprint • Produce and capture methane gas • Able to retain biomass in the reactor for higher organic loading treatment	• Poor separation between treated effluent and biomass	[25]
Ponding system	• Low cost • Less/no maintenance needed	• Large land area required • Long HRT (> 50 days) • Direct release of methane and hydrogen sulphide to environment • Poor separation between treated effluent and biomass	[29]
Upflow anaerobic sludge blanket (UASB)	• Small footprint • Produce and capture methane gas	• Unable to retain biomass for higher organic loading treatment • Poor separation between treated effluent and biomass	[30]
Aerobic digestion	• No formation of pollution-causing gases	• High energy for aeration required to breakdown the organic content of POME • Poor separation between treated effluent and biomass	[32]
Ozone-anaerobic digestion integrated system	• Efficient in converting recalcitrant pollutants into biodegradable organics	• Costly treatment method	[42]
Aerobic-anaerobic integrated system	• Small footprint • Can treat high organic loading of POME	• Poor separation between the treated effluent and biomass	[42]
Anaerobic-filtration integrated system	• Capable of treating high organic loading of POME	• Requires frequent maintenance to sustain desirable product	[43]
Coagulation–flocculation	• Low cost	• Removes only suspended solids and residual oil • Release of residual elements from coagulant pollutes water	[45]
Sequencing batch reactor – aerobic granules	• No formation of pollution causing gases • Excellent separation between treated effluent and biomass • Small footprint • Able to be operated at higher loading rate	• High energy for aeration is required to breakdown the organic content of POME • No production of methane	[46]

marketable by-products could achieve zero discharge for the treatment plants and simultaneously contribute towards sustainability. Thus, screening of the possible by-products from the various treatment methods is a prerequisite.

3. By-products of POME treatment systems

Various types of by-products are generated while treating POME. Some of the by-products are extremely undervalued, and consequently, their economic potential remains untapped. Very little research has been devoted towards research into the further utilisation of these by-products. By-products produced to date from various forms of POME treatment methods and their potential to replace existing products are given in Table 4.

3.1. Gas by-products

From Table 4, methane gas is one of the common by-products produced from the treatment methods. Methane has been proven to be an energy source to power the mill [50]. The utilisation of methane gas to produce electricity will directly reduce the overall production cost of CPO. However, not all the palm oil mills have the facility to convert the methane energy source into electricity. As a result, the potential of the methane gas is not used at all. Apart from methane gas, hydrogen gas could also be produced from the anaerobic treatment plant. Biohydrogen is formed during the acidogenic fermentation of wastewater [46]. During the acidogenesis process, volatile fatty acids (VFAs) and biohydrogen gas are produced. However, these VFAs will not be converted into methane gas due to the inhibition of the methanogenesis process (a process to produce methane gas). Lower pH value (below 6) and higher temperature (above 60 °C) in the reactor inhibit the methanogenesis process.

3.2. Solid by-products

As depicted in Table 4, waste sludge is another by-product of the wastewater treatment plant. Research on waste sludge is quite sporadic, and the growing amount of sludge needs serious attention. Generally, waste activated sludge from various sources of wastewater has been used as adsorbent to remove textile dyes [51,52] or used as fertiliser [22]. The adsorption capacity of the waste-activated sludge is shown in Table 5. Tsai et al. [53] have reported that commercial activated carbon has an adsorption capacity of 373 mg/g for chloroform adsorption. Table 5 clearly shows that the adsorption capacity of waste-activated sludge is comparable to that of commercial activated carbon. Waste sludge is applicable as an adsorbent due to the naturally occurring functional groups on the surface [51]. Waste sludge aids the adsorption process via physical and chemical adsorption methods. Meanwhile, waste aerobic granules are produced from SBR. Excess aerobic granules in SBR are wasted to retain the balance of the food to microorganism ratio and to maintain solid retention times. The wasted aerobic granules are still active biomass that could be re-used for other purposes.

Based on the 2012 market price, PHA has the highest market value of all of the by-products (Table 4). The reason for the expense is the cost of the raw materials used to produce PHA. As a result, the applicability of PHA is limited, and the market is continually being flooded with cheaper petroleum-based plastics. The market price of PHA is approximately 20–80% higher compared to conventional petroleum-based plastics [57]. Production of PHA from waste streams is highly welcomed to reduce the market price and make the production of PHA competitive with the petroleum-based plastics. Mass production of PHA from waste streams would reduce the reliance on conventional plastics. From the perspective of an investor, PHA production from waste streams provides an additional income to the overall plant operation.

In 2012, the estimated release of POME was approximately 58 million tonnes (based on the CPO production). By envisaging the yield of PHA production to be 0.257 t PHA/t substrate (similar to Chakravarty et al. [58]), POME is capable of producing approximately 2.5 million tonnes of PHA annually (based on the average COD value of POME). Use of POME as a carbon substrate and high volume of PHA production would lower the price of PHA and eventually expand the use of PHA. The estimated PHA production and its income are summarised in Table 6. On average, the estimated annual income for each palm oil mill in Malaysia is projected to be around RM 10.75 million. This gross income looks very appealing. Apparently, the annual net revenue is expected to be around RM 4.3 million (40% of the total income) after considering the tax and operating cost. Hence, PHA production from POME can be considered as a profitable venture for the investors.

Table 5
Utilization of sludge as adsorbent.

Adsorbent	Adsorption capacity (mg/g)	Reference
Methylene Blue	66.23	[51]
Reactive Black 5	93.00	[54]
Methylene Blue	130.69	[52]
Chloroform	244.00	[53]
Toluene	350.00	[55]
Phenol	100.00	[56]
Rhodamine	33.33	[56]

Table 4
By-products of various POME treatment methods.

POME treatment method	Valuable by-product	Potential use(s) for	Market price of potential product (RM)	Reference
UASB	• Waste anaerobic granular sludge	• Activated carbon	1.68–6.01/kg[a]	[25]
	• Biohydrogen	• Power generation	0.32/kW h[b]	
	• Methane gas	• Power generation	0.32/kW h[b]	
	• Volatile fatty acid	• PHA feedstock	–	
Aerobic digestion	• Waste activated sludge	• Activated carbon	1.68–6.01/kg[a]	[32]
Sequencing Batch Reactor	• Waste aerobic granules	• Activated carbon	1.68–6.01/kg[a]	[20]
		• PHA synthesis	14.1–19.37/kg[c]	
	• Biohydrogen	• Power generation	0.32/kW h[b]	
Membrane Technology	• Water	• Boiler feed	–	[23]
	• Methane gas	• Power generation	0.32/kW h[b]	

1USD=RM 3.19 (as on 19th July 2013).
[a] Gongyi City Xianke Water Supply Material Co., Ltd. [47].
[b] Feed-In-Tariff (FiT) rates for biogas [48].
[c] Bioplastic development increases with new applications [49].

Moreover, this projected amount of PHA is estimated to reduce the dependence on petroleum-based plastics by at least 50%. However, this projected value is achievable only with proper regulation of operating parameters. As mentioned in Table 4, aerobic granules could be used to accumulate PHA inside its cells. Research attempting re-use of waste aerobic granules for PHA accumulation is discussed in the following section.

4. Waste aerobic granules

4.1. General structure of aerobic granules

Aerobic granules differ from waste activated sludge in terms of morphology, robustness and performance [34,61]. Fig. 5(i) and (ii) clearly exhibits the morphological difference between activated sludge and aerobic granules. The mechanism of formation of aerobic granules is shown in Fig. 6. Because the aerobic granules originated from activated sludge, the aerobic granules inherit the microbial behaviour of activated sludge. The aerobic granules formed are compact and denser. Hence, aerobic granules have better settling ability compared to conventional activated sludge [62]. The good settling ability of aerobic granules makes the effluent free of residual biomass. The use of clarifier could therefore be eliminated, making the treatment area smaller. This minimisation of the treatment area is one of the reasons for the application of granulation technology to increase at wastewater treatment plants in recent years.

Table 6
Estimated production of PHA and projected gross income.

Input	Parameter	Unit	Value
A	CPO production[a]	Tonne	18,785,030
B	POME production[b]	m^3	58,703,218.75
C	COD in POME[c]	kg/m^3	51
D	Estimated COD[d]	kg COD	2,544,784,533
E	PHA yield[e]	kg PHA/kg COD	0.257
F	PHA production[f]	kg PHA	654,009,624.9
G	Price of PHA[g]	RM/kg	7.00
H	Estimated gross PHA price[h]	RM	4,578,067,375.00
I	Number of palm oil mill in Malaysia		430
J	Estimated average annual income for each palm oil mill[i]	RM	10,646,668.31

[a] Based on statistics reported by Malaysian Palm Oil Board [59].
[b] Assume 3.125 m^3 of POME produced for every 1 t of CPO production.
[c] Average COD value of POME [60].
[d] Efficiency of COD conversion is assumed to be 85% (D=0.85*B*C).
[e] PHA yield is assumed to be similar to Chakravarty et al. [58].
[f] (F=D*E).
[g] Price of PHA is assumed to be half of the current price with the envisaged escalation in PHA production.
[h] (H=F*G).
[i] (J=H/I).

4.2. Mechanism of action of aerobic granules applied to the treatment of wastewater

Like conventional activated sludge, the aerobic granules will consume the biodegradable organic content of the wastewater for both growth and maintenance. In conventional activated sludge, after each cycle of substrate feeding, some portion of the consumed organic content will be stored as polyhydroxyalkanoate (PHA) inside the cells of microorganisms. PHA functions as the energy storage material which will be used during famine periods [64]. In aerobic granules, PHA accumulation has been reported previously [65,66]. However, a sole focus on extracting PHA from aerobic granules has thus far not been done.

4.3. Formation of aerobic granules in POME

Formation of aerobic granules in POME has been reported by Abdullah et al. [67] and Gobi et al. [20]. In both of the papers, the aerobic granules were reported to be formed inside the sequencing batch reactor with POME as the substrate. The maturation period of the aerobic granules as reported in the two research papers differs. A period of 120 days was required for Gobi et al. [20], while the maturation period was only approximately 60 days in the work done by Abdullah et al. [67]. The difference is presumably due to the different exchange ratios and reactor configurations. In both of the papers, the amount of COD removed was approximately 90%. These research efforts prove that aerobic granules could be developed in POME.

4.4. Generation of waste aerobic granules

The growth process of aerobic granules has led to the presence of excess aerobic granules in SBR. To maintain sludge retention time (SRT) inside the reactor, some of the excess aerobic granules must be wasted. Rather than just disposing of the waste aerobic granules, they could be re-used for some other purposes. The re-use of the excess aerobic granules is basically unexploited as only a handful of researchers have reported on the growth process of aerobic granules in the literature to date.

4.4.1. Application of waste aerobic granules

Gao et al. [68] have used inactive aerobic granules for the adsorption of Yellow 2G and Reactive Brilliant Red K-2G. The biosorption capacity of the aerobic granules has been reported as 58.50 and 66.18 mg g^{-1} for Yellow 2G and Reactive Brilliant Red K-2G,

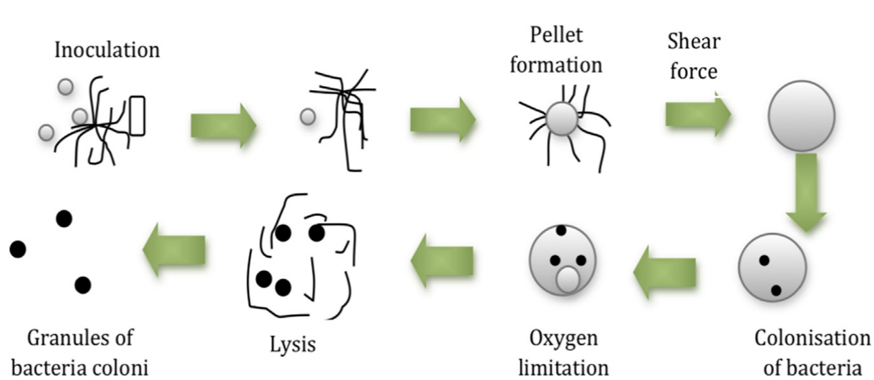

Fig. 6. Formation of aerobic granules from activated sludge [63].

respectively. Gobi et al. [20] have used inactive aerobic granules to adsorb remaining COD and to reduce the turbidity of POME treated in SBR. The removal percentage of the remaining COD and turbidity is reported as 21% and 99%, respectively. The two papers indicate that aerobic granules can be useful as adsorbents.

Aerobic granules have also been used as seed sludge to develop aerobic granules in a new reactor. Pijuan et al. [69] have used crushed aerobic granules as seed sludge to reduce the startup time of the reactor. Only 18 days were required for the aerobic granules to develop [69]. The time required was far less compared to 120 days in the work of Gobi et al. [20] using activated sludge as the seed sludge. The time difference can probably be explained by the fact that some portion of the crushed aerobic granules remained intact. As a result, the crushed aerobic granules enhanced the attachment of the floccular sludge on the crushed aerobic granules. This phenomenon has resulted in faster development of aerobic granules, simultaneously reducing the startup time of the reactor. This novel method reduced the startup time of the reactor without altering the dimensions or changing the operating parameters of the reactor. In another research effort, Wang et al. [70] have used broken aerobic granular sludge to produce a nitrobenzene-degrading bacterium (*Klebsiella ornithinolytica NB1*). The biodegradation rate of nitrobenzene reached 9.29 mg L^{-1} h^{-1} with the use of that bacterium.

However, of all the re-utilisation schemes for aerobic granules, the most attractive use of aerobic granules is to produce PHA. The synthesis of PHA has been overlooked because PHA is an intermediate product. Thus, the challenge of the upcoming research would be finding a way to promote bulk production of PHA in aerobic granules (by using POME as the substrate) and subsequently using PHA as a substitute for the petroleum-based plastics. This substitution, if it could be accomplished, would significantly reduce the dependence on the non-sustainable petroleum-based biopolymer and simultaneously promote green technology.

5. Polyhydroxyalkanoate (PHA)

5.1. Production mechanism

Polyhydroxyalkanoate (PHA) is an energy storage molecule accumulated naturally inside microorganisms [71]. PHA is a common term that refers to the total accumulation of monomers such as hydroxybutrate (HB) and 3-hydroxyvalerate (3HB-3HV), 3-hydroxyvalerate (3HV), 3-hydroxy-2-methylvalerate (3H2MV) or 3-hydroxyhexanoate (3HHx) [72]. PHA can generally be classified according to the carbon chain length, either short chain length (SCL) or medium chain length (MCL). The general chemical structure of the PHA is shown in Fig. 7. PHA is a readily biodegradable and biocompatible polymer with properties almost similar to conventional plastics [73]. However, commercialisation of PHA is hindered by the high substrate cost as well as the non-sustainable nature of the feedstock [74]. Researchers found that waste streams rich in carbon sources could be used as a substrate to produce PHA [75]. Various types of wastes such as olive oil mill effluent, sugar molasses and food waste have been used as the substrate to produce PHA [76,77]. The PHA accumulation profile in a mixed culture is shown in Fig. 8. Fig. 8 shows that the accumulation of PHA occurs during the feast period with concurrent reduction of carbon content. A similar trend will be observed in any other mixed culture used to accumulate PHA.

In wastewater, PHA will be accumulated inside the microorganisms by taking up the available volatile fatty acid (VFA). Production of PHA has been reported to be higher in fermented substrates rather than an unfermented carbon source [77]. The fermented substrate possibly contains a higher proportion of VFA, which has a shorter chain length. The PHA accumulating microorganism can more easily take up the VFA rather than a complex substrate. Wastewater will generally undergo acidogenic fermentation to produce VFA. The VFA is then fed into a reactor that contains PHA-accumulating organisms. VFA will be transformed into the respective acyl-CoA and subsequently converted into PHA by the organisms present in the reactor [80]. The common equations for PHA production from various carbon sources are summarised in as follows [81]:

$$\Delta\text{Carbon substrate} + \Delta\text{Carbohydrate} = \Delta P(\text{HB/HV}) + \Delta\text{Active biomass} + \Delta\text{Soluble microbial products} + \Delta CO_2 \quad (1)$$

To accumulate PHA inside the microorganisms, operating conditions play a vital role. Aerobic dynamic feeding (ADF) is the conventional approach adopted by the researchers to accumulate PHA inside cells. In ADF, feast and famine phase will be established in the reactor. ADF suppresses the internal growth of the microorganism, thus forcing the microorganism to adapt itself to the limitation of nutrients arising from ADF. During the adaptation period, the substrate will be stored as PHA inside the cells of microorganism [82]. Gao et al. [83] recently illustrated the overall pathway of PHA production clearly, and this pathway is shown in Fig. 9. Although an overall idea of PHA accumulation inside the microorganisms were established, PHA accumulation inside the microorganisms is mainly applicable to pure culture methods only. With a comprehensive understanding of the accumulation in the pure culture method, approximately 86% CDW PHA was accumulated inside microorganisms [84]. However, similar amounts of PHA accumulation were not accomplished inside mixed culture microorganisms. As viewed from an economic perspective, a mixed culture method is more feasible to be applied at the industrial level rather than a pure culture method [79,85]. Current research therefore focuses on PHA production via mixed culture microorganisms [73,77].

5.2. Production of PHA via mixed culture

A mixed culture method of producing PHA offers a good solution to the high cost of a pure culture method [86]. However, the major problem of this mixed culture method is poor accumulation of PHA inside the microorganism [79]. Though myriads of microorganisms are present in the mixed culture, not all of the microorganisms can function to accumulate PHA inside their cells. The researchers therefore came up with a solution by enriching the PHA-accumulating microorganisms in the mixed culture system [76,86]. Just by altering the operating conditions of the reactor, microbial communities that are highly enriched in PHA-accumulating organisms could be cultured.

However, in a mixed culture method, the challenge would be ceasing the inhibition of the PHA accumulation process. Johnson et al. [87] recently studied the effect of ammonium on PHA accumulation in a mixed culture and found that only 69 wt% of PHA was accumulated under conditions of excess ammonium after 4.4 h.

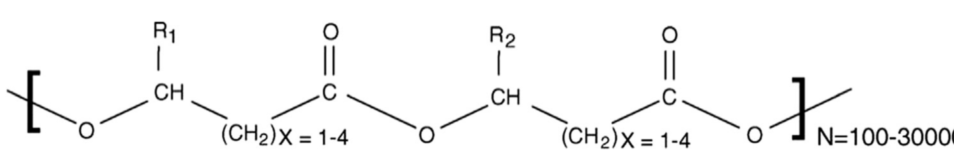

Fig. 7. General chemical structure of polyhydroxyalkanoates. R1 and R2 are alkyl groups (C1–C13) [78].

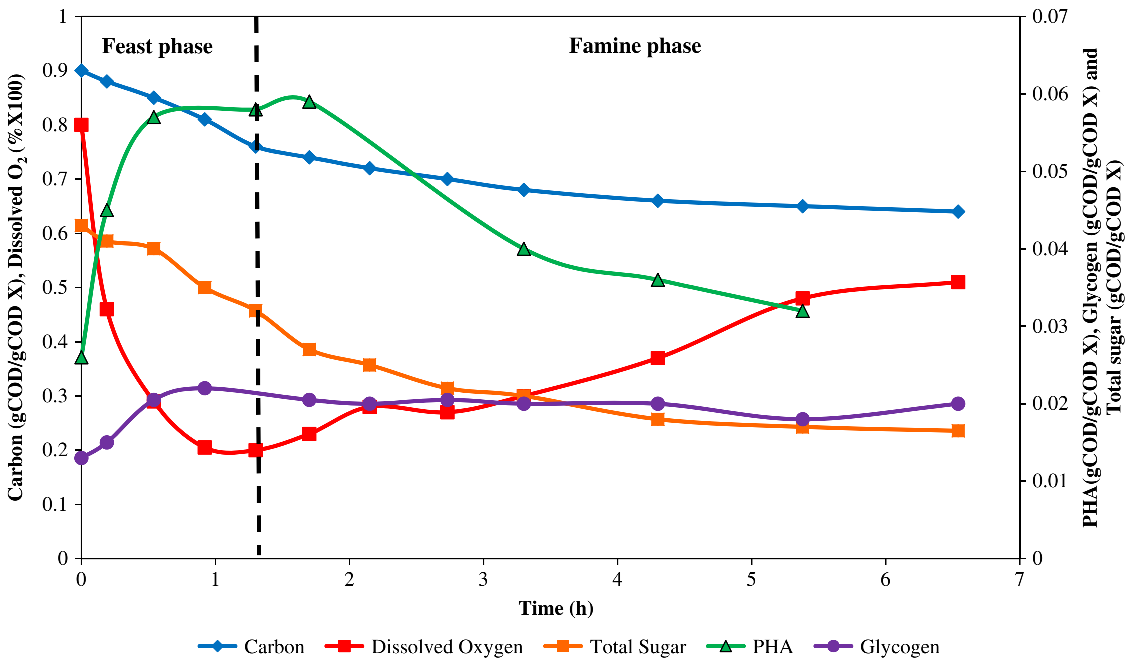

Fig. 8. PHA accumulation profile in a mixed culture [79].

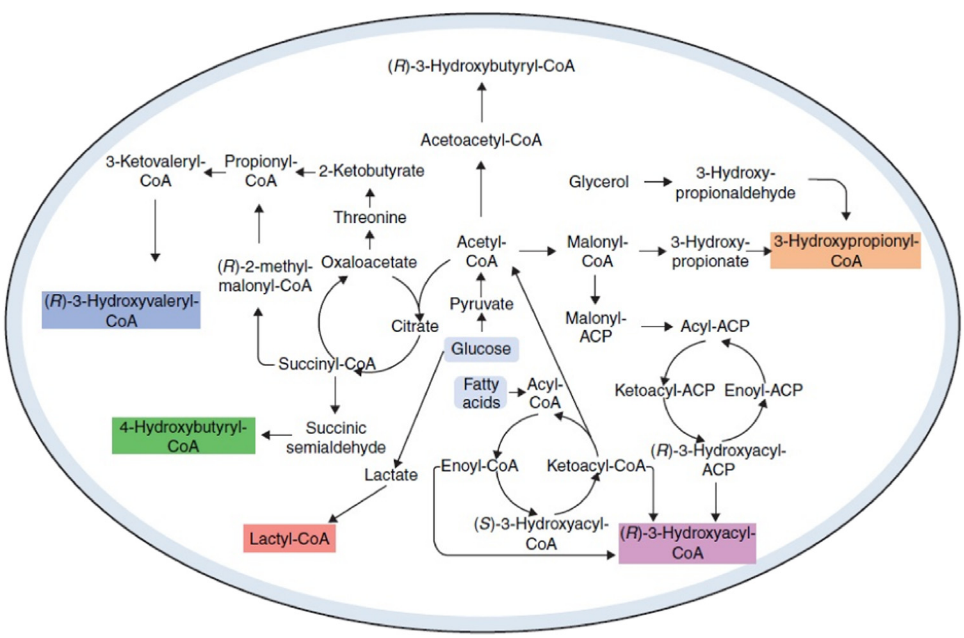

Fig. 9. Overall pathway of PHA production [83].

Serafim et al. [88] found that when 180 Cmmol/L acetate was fed in one single pulse, the acetate causes inhibition of the accumulation of PHA, and eventually only 67.5% of the cell dry weight of PHA could be accumulated. High level inhibition due to substrate is believed to result in production costs similar to the pure culture method, which nullifies the objective of using the mixed culture method. Moreover, inhibition will result in high production costs due to the recovery of small amounts of PHA accumulated inside the microorganisms. Inhibition factors ranging from operating conditions, excess nutrients, limitation of nutrients and thermodynamic effects have been studied for their effect on PHA accumulation [73,87,89,90]. These parameters were reported to inhibit the PHA accumulation to various degrees.

5.3. *Recent trend of producing PHA via mixed culture*

Development of a mixed culture method to produce PHA has paved the way for the utilisation of waste streams rich in organic content to be used as a carbon substrate. Wastewaters from sources such as sugar molasses [73], olive oil pomace [91], food waste [92], and POME [93] have been used successfully as carbon substrates for PHA production. One of the key issues that need to be addressed with the mixed culture method is the lower amount of PHA accumulation compared to the pure culture method [76]. To enhance the amount of PHA in the mixed culture, attention has been focused on the enrichment of the PHA-accumulating organism. As a fundamental step towards enrichment of the PHA-accumulating organism,

a feast-famine period has been established. In the work done by Albuquerque et al. [94], a feast-famine ratio of 0.5 and 0.22 yields 0.18 and 0.59 Cmol PHA/Cmol VFA, respectively, clearly indicating that a lower feast-famine ratio would spur the PHA yield. This eco-biotechnology method was first reported by Johnson et al. [86] in their attempt to match the PHA yield of engineered bacteria. This breakthrough has been the stimulant to produce PHA in a continuous mode reactor. Chakravarty et al. [58] have reported the production of PHA in a continuous mode reactor, where the yield of PHA was between 0.213 and 0.257 g PHA/g acetate. Ideally, the methodology used in the continuous mode reactor is applicable to all other wastewaters as well. Enrichment of the PHA-accumulating organism and successful operation of the continuous mode reactor could be the way forward to commercialise the PHA production from wastewater in the future. The ways to apply this technology to POME must be explored. To be able to apply this technology to POME, the recent trend for PHA produced from POME has to be understood.

6. PHA accumulation using POME

6.1. Composition of POME

To date, several papers have reported the production of PHA from POME [84,93]. As Table 1 shows, POME is very rich in biodegradable organic content. Anaerobically digested POME will convert the biodegradable organic content into volatile fatty acids (VFAs). VFAs function as the carbon substrate for PHA production. Complete anaerobic digestion of POME will generally result in production of methane and CO_2 [27]. A complete anaerobic digestion consists of three theoretical stages. Hydrolysis, acidogenesis, and methanogenesis are the three stages involved in producing methane and CO_2 [27]. When the anaerobic process is stopped at the acidogenesis stage, the process will yield only VFA and biohydrogen. The common VFAs produced are acetic, propionic, butyric, and isobutyric acids [95,96]. VFA composition will eventually determine the type of PHA formation [97]. Theoretically, in POME, a wide range of PHAs such as 3-hydroxybutyrate, 3-hydroxyvalerate (3HV) and 3-hydroxy-2-methyl valerate (3H2MV) could be formed from the constituents of VFA.

6.2. PHA-accumulating microorganisms

PHA-accumulating microorganisms will take up the available VFA and store it inside the cells. These microorganisms possess the enzymes to turn the VFA into PHA by a specific pathway. Due to their high accumulating ability, the pure culture method has been the preferred method over mixed culture. PHA quantity is calculated in terms of PHA content (% of cell dry weight). In the work of Mumtaz et al. [84], *Comamonas sp. EB172* (microorganism species) has been used to produce the PHA. Cell dry weight with 90% PHA was reported in this work. *Comamonas sp. EB172* has the ability to accumulate the PHA with high purity when the operating parameters favour the accumulation of PHA. Meanwhile, in the work of Hassan et al. [98], the PHA has been produced using *Rhodobacter sphaeroides*, a photosynthetic bacterium which functions to produce the PHA from the VFAs. PHA is accumulated up to 30% of the dry cell weight of the bacteria. Meanwhile, Alias and Tan [99] were able to isolate two types of bacterium that could utilise palm olein for PHA synthesis. The FLP1 and FLP2 used have managed to accumulate PHA up to 18.6% of the cell dry weight [99]. The massive difference in PHA accumulation in the work done by Mumtaz et al. [84] and Alias and Tan [99] is the substrate used for PHA accumulation. Mumtaz et al. [84] used a higher percentage of VFA resulting from the anaerobic process. The higher percentage of organic acid enabled the *Comamonas sp. EB172* to wholly use the VFA available to convert the VFA into PHA. Apart from the pure culture method, recently Md. Din et al. [93] studied PHA production using the mixed culture method. A partially high yield (0.8 Cmol/Cmol acetate) has been reported for a mixed culture method. This development could be the 'game changer' for producing the PHA in POME commercially. However, this development is still in the beginning stages and requires more studies before commercialisation.

6.3. Quantity of PHA produced

Though numbers of research studies have been dedicated to PHA production using POME, the yield reported from these studies has yet to match other wastewaters [76]. Table 7 exhibits the microorganism used for PHA accumulation and its respective yield and PHA content. The low yield observed for pure culture method in Table 7 indicates that the available organic content was not channelled towards PHA production, possibly due to the complexity of the VFAs produced in POME or the limitation within the microorganisms used to accumulate PHA using POME. The limitation of the microorganisms could be overcome by selecting a superior microorganism with high selectively towards PHA accumulation. A higher percentage of cell dry weight would be economically feasible for an extraction process. Nevertheless, a significant surge in terms of PHA content has been found between the earlier work done by Hassan et al. [100] and the work recently performed by Mumtaz et al. [84].

7. Biohydrogen generation using POME

The literature reveals that biohydrogen has been generated successfully from the POME treatment process [101]. Biohydrogen has been generated from the POME using either pure culture strains or mixed culture bacteria. The maximum yield of biohydrogen in pure culture [101] and mixed culture [102] was 31.95 mL H_2/g COD and 4708 mL H_2/L-POME, respectively. Mixed culture appears to offer a better option for the production of biohydrogen than pure culture in POME. Previous research using POME for biohydrogen production and the results are shown in Table 8.

Biohydrogen is highly regarded as a potential fuel in the future, especially in a carbon-free energy system [103]. Attention has been given to the biohydrogen because biohydrogen can generate a higher energy yield compared to fossil fuels. Hence, the production of biohydrogen has been extensively researched from various perspectives in recent years [17,101]. These studies attempt to combat the high storage and production costs, which are the hindrance to the commercialisation of biohydrogen [104]. Biohydrogen could be generated via several pathways such as dark fermentation, photofermentation, a two-stage process (integration of dark- and photofermentation) and biocatalysed electrolysis [105]. However, dark fermentation is reported to be the most feasible pathway to produce biohydrogen because dark fermentation has a high rate of cell growth, requires no light energy, has no oxygen limitation problems and requires a lower capital cost [104]. During the dark fermentation process, the fermentation process has to be stopped at the acidogenesis process to promote the collection of biohydrogen. Failure to stop the methanogenesis step will result in further degradation of the dark fermentation product which also includes the biohydrogen gas generated in the acidogenesis stage. The production mechanism for biohydrogen is shown in the following equation:

$$C_6H_{12}O_6 + 2H_2O = 2CH_3COOH + 2CO_2 + 4H_2 \quad (2)$$

Temperature plays an important role in biohydrogen generation. Table 8 shows the microbial species specifically identified

Table 7
PHA production in POME.

Microorganism	Type of microorganism	PHA yield	PHA content (% cell dry weight)	Reference
Comamonas sp. EB172	Pure culture	0.31	85.8	[84]
Rhodobacter sphaeroides	Pure culture	0.5	67.0	[98]
Burkholderia cepacia	Pure culture	NA	57.4	[99]
Alcaligenes eutrophus	Pure culture	0.32	45.0	[100]
Heterotrophic aerobic bacterium and activated sludge	Mixed culture	0.80[a]	74.0	[93]

NA – not available.
[a] C-mol/C-mol acetic acid (HAc).

Table 8
Production of biohydrogen from POME.

Medium	H_2 production rate (mL H_2/L-POME)	Reference
Clostridium butyricum EB6	31.95	[101]
Anaerobic sludge	4708	[102]
Microflora	102.6	[106]
Thermophilic microflora	4.4[a]	[107]
Thermoanaerobacterium thermosaccharolyticum	4800	[108]
Rhodopseudomonas palustris PBUM001	1050	[109]
Thermoanaerobacterium	4200	[110]
Anaerobic mixed microflora	6700	[111]
Thermotolerant consortia	702.52	[112]
Mixed culture	144.00	[96]
Mixed culture	589.00	[113]
Mixed culture	2640[a]	[114]

[a] (mL H_2/L-POME. day).

with their temperature tag (thermophilic and mesophilic). Biohydrogen generation is highly favourable in the thermophilic region (approximately 60 °C). At this temperature, the activity of the methanogens will be inhibited, and this inhibition will promote the production of biohydrogen. In a nutshell, biohydrogen is a by-product that can be generated in large amounts by using POME. However, to date, the applications of biohydrogen are very limited. Biohydrogen generation can therefore be coupled with PHA production at the POME treatment plant for the benefit of the palm oil mill. Reliance on biohydrogen and PHA could contribute significantly towards green technology and sustainability. However, some constraints need to be addressed before implementation of these by-products could be commercialised.

8. Constraints in PHA and biohydrogen production

8.1. PHA from POME

The papers on PHA production from POME indicate some persistent problems that must be addressed before upscaling PHA production from POME to the industrial level. First and foremost, the pure culture method has been used to produce PHA inside the microorganisms. This methodology is very fragile and incurs a high cost for implementation at the industrial level [86]. Moreover, this method is very sensitive towards environmental changes as well as the operating parameters of a reactor. Though the pure culture method could give high yield in terms of PHA accumulation, the pure culture method is always susceptible to failure on a large scale. The mixed culture method is very much at the beginning stages for large scale implementation. Further studies are required for comprehensive understanding of PHA accumulation using a mixed culture. Most significantly, inhibition factors in the mixed culture must be studied extensively before overall conclusions can be drawn regarding commercialisation.

Proper modelling of the PHA production has yet to be done. Modelling of a process is essential in upscaling the process to the industrial level. Modelling of PHA production should include inhibitory effects of operating parameters on PHA production and the importance of the composition of VFAs. The interaction between these parameters would be useful in determining the yield of the PHA. Once all these factors are scrutinised, a comprehensive model might be developed for PHA production from POME.

Another obvious challenge is producing the PHA in a continuous mode rather than in batches. Currently, no attempts have been made to study the feasibility of the PHA production in a continuous mode using POME. Only a handful of papers have been produced using this technique for another source of wastewater [58]. The main problem is determining the retention time of the POME at each stage of the operation. Adequate time is needed for the organic acids to be synthesised at the acidogenesis process for PHA production in microorganisms. Perhaps, if adequate retention time could be found in the POME treatment plant for PHA production, the chances of this method to be implemented at industrial level would be enhanced.

PHA production also faces problem in terms of a non-sustainable extraction process. Thus far, a halogenated method has been in use for the extraction of PHA [115]. Hazardous chemicals such as chloroform and sodium hypochlorite, which are necessary for the halogenated method, are not feasible for commercial use. Moreover, a complex treatment system would be required to remove the hazardous solvents once PHA has been extracted. Recent work on an eco-friendly PHA recovery system was reported by Mohammadi et al. [115]. However, this method requires further study to ensure that a higher purity of PHA is recovered. Moreover, PHA accumulated inside aerobic granules might require a complex mechanism for the recovery process.

8.2. Biohydrogen from POME

The production of biohydrogen from POME is yet to be commercialised due to several factors. Most commonly, the biohydrogen-producing microorganism must be dominant in the mixed culture medium of the POME treatment plant to ensure the maximum production of hydrogen from the anaerobically digested POME. *Clostridium sp.* and *Enterobacter sp.* have been identified as hydrogen-producing bacteria [116]. However, the methods for enriching these species through manipulation of the operating parameters of the reactor have yet to be identified. Current methods of enriching these species of bacteria are costly and not feasible to be implemented at the industrial level.

Biohydrogen is a product of the acidogenesis process. In the acidogenesis process, the volatile fatty acids (VFAs) are produced at a higher proportion. These VFAs will cause the pH to decrease and consequently make the mixed liquor acidic. This phenomenon

is indeed an inhibitor for the production of biohydrogen [117]. Previous work has demonstrated that the optimum pH for biohydrogen production from wastewater is 5.5 [118]. To ensure optimum biohydrogen production, a balance between adequate VFA production and the pH of the mixed liquor must be found. VFA production could not be compromised merely for the sake of biohydrogen generation as VFA is important for the accumulation of PHA.

The generation of biohydrogen in a continuous mode is an another challenge that must be addressed. Ideally, continuous generation of biohydrogen is highly desired in a wastewater treatment plant to ensure the chain of energy supply for the treatment plant or trading purposes. However, few have reported on the continuous generation of biohydrogen in the wastewater treatment plant, let alone a POME treatment plant.

9. Future work

From this review, production of PHA in waste aerobic granules is evidently one method to transform a wastewater treatment plant into a revenue-generation platform. This transformation would ensure the release of cleaner wastewater and at the same time, the palm oil mill would be able to operate sustainably. As a first step, aerobic granules should be formed on a pilot plant scale SBR by using POME. Later, the wasted aerobic granules can be used as a medium to accumulate PHA inside the cells with fermented POME as the carbon source. PHA, POME and aerobic granules have previously been studied as separate entities, and promising results were obtained from those studies [20,93]. Later, a continuous mode reactor must be designed to ensure that PHA accumulation could occur at the same HRT of the wastewater. This exclusive design of the reactor setup requires extensive detailing before the process could be further upscaled. Comprehensive studies on the inhibition process, optimum conditions for PHA accumulation in waste aerobic granules and a sustainable PHA recovery process are critically needed to ensure the success of this treatment system. The inhibition may be caused by the presence of various non-accumulating microorganisms, the operating parameters of the reactor or the predators present in the POME. Therefore, the need to analyse the inhibitory mechanism and its effect on PHA accumulation is critically needed if this technology is to be transformed to the industrial scale. Efforts must be dedicated towards finding a higher yield of PHA production per unit of POME treated. These aforementioned steps are the fundamentals in producing the PHA on a large scale by using waste aerobic granules.

Biohydrogen production can be coupled with the PHA accumulation as the revenue-generating source of a POME treatment plant. Biohydrogen production lies in the pathway of PHA production, so the need for any additional processes for biohydrogen generation may be eliminated. It is therefore a win-win situation for the production of biohydrogen and PHA accumulation in bulk amounts. To make the palm oil mill sustainable, the opportunity of using the biohydrogen gas as a power source should not be ignored. The biohydrogen produced could power the palm oil mill, and at the same time, the waste of an energy source could be avoided. Moreover, using the biohydrogen gas as a power source will reduce the dependence on the national grid for electricity and if there is any surplus of electricity generated, surplus electricity could be sold to the national power grid or utility companies [119]. Another source of income could be tapped for maximum usage.

Modelling also plays an important role in the transformation of this technology from laboratory scale to pilot and industrial scale. Thus, the development of models for PHA production in an aerobic granular system is highly desired. Modelling could first be done for the pilot plant scale PHA production using waste aerobic granules. The main focus has to be given to the yield of the PHA accumulation inside the waste aerobic granules. Unforeseen circumstances such as presence of toxic material inside the wastewater should be considered during the modelling process. A complete model would aid the upscaling process significantly.

In depth cost analysis of the PHA and biohydrogen production using aerobic granules in SBR is critically needed. In depth cost analysis would provide an all-inclusive knowledge about the economic feasibility of PHA production using aerobic granules in an SBR treating POME. PHA produced in aerobic granules could be able to generate profit with the use of SBR technology. However, application of SBR technology to the POME treatment itself is very rare. The cost analysis for PHA production in an SBR treating POME on the industrial level is difficult (almost impossible). Thorough cost analysis using pilot plant scale SBR would help to estimate the overall operating cost and subsequently determine the return of investment. Envisaging the potential of the aerobic granules, the POME wastewater treatment plant could be a real 'gold mine' if this method could be implemented in the future.

10. Conclusion

By-products of the POME treatment plant, especially PHA and biohydrogen, have a major potential to be commercialised. Commercialisation of PHA and biohydrogen would offer a return of investment as well as zero discharge from the POME treatment plant. Methods to enhance the productivity must be developed and implemented. PHA production from a POME treatment plant could be given attention as PHA production from a POME treatment plant has high market value and is sustainable. This naturally forming PHA could be commercialised by proper mitigation of operating parameters and via comprehensive understanding of the entire accumulation mechanism. Biohydrogen production would also generate income for the treatment plant. In tandem with these findings, SBR technology using aerobic granules should be studied extensively because SBR technology using aerobic granules is able to produce both PHA and biohydrogen as the by-product while maintaining its primary role to treat POME efficiently. Adoption of this technology at the industrial level is expected to pique the interest of the mill operators to invest in new technologies for a wastewater treatment plant.

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